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Electron Spin Resonance Study of Radiation- and Free Radical-Induced Reactions of Methylenecycloalkanes

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Methylenecycloalkane free radicals are studied by electron spin resonance method at -196°C . Free radicals are formed by four ways; electron-irradiation, ultraviolet-irradiation, reaction with methyl radicals and reaction with hydroxy radicals. The observed electron spin resonance spectra are assigned and discussion is made on the mechanism of free radical formation reactions. For methylenecyclopropane and methylenecyclobutane, the alkane ring opening reaction plays an important role, whereas methylenecyclopentane radical is formed only through the abstraction of the hydrogen atom from the alkane ring. The four ways of radical formation are divided into two groups, each of which brings about the different types of free radicals.

INTRODUCTION

We have ever studied free radicals formed from conjugated dienes through four different ways; (a) irradiation with fast electrons, (b) irradiation with ultraviolet lights, (c) reaction with methyl radicals, and (d) reaction with hydroxy radicals. It was found that different free radicals were obtained from the different ways of radical formation.¹⁾ In the present investigation, free radicals formed from methylenecycloalkanes, $\text{CH}_2=\text{C}(\text{CH}_2)_n$ ($n=2, 3, 4$), through the four ways are studied by electron spin resonance (ESR) method.

Methylenecycloalkanes have a strained alkane ring together with a double bond attached to the ring. It is expected that the mechanism of free radical formation may be affected by the number of the alkane ring member.

EXPERIMENTAL

Methylenecycloalkane, the purity of which is more than 99%, was used after being dried with calcium hydride. Concentrated hydrogen peroxide is prepared by distillation of commercial 30% aqueous solution. Methyl iodide was purified by distillation and dried with calcium hydride. These materials were distilled into a glass or quartz ESR ampoule through the vacuum line and the sample tube was sealed at about 10^{-4} mm Hg.

Irradiations of pure methylenecycloalkanes with fast electrons were carried out by a van de Graaff accelerator (1.5 Mev) for a few Mrad at -196°C . Irradia-

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tions of pure methylenecycloalkanes in quartz tube with ultraviolet lights were carried out by a medium pressure mercury lamp, the emission spectrum of which had a intense peak at 2537\AA . Reactions of methylenecycloalkanes with methyl radicals were brought about by irradiating a methylenecycloalkane sample with a small amount of methyl iodide with high pressure mercury lamp at -196°C . Reactions of methylenecycloalkanes by hydroxy radicals were brought about by irradiating a methylenecycloalkane sample with a small amount of concentrated hydrogenperoxide in the same way as mentioned above. Pure methylenecycloalkanes gave no ESR signal when illuminated by the high pressure mercury lamp, therefore ESR spectra observed from the mixture of methylenecycloalkane and methyl iodide or hydrogenperoxide are due to free radicals formed by the reaction between methylenecycloalkane and photo-produced methyl radicals (or iodine atom) or hydroxy radicals.

ESR measurements were all carried out at -196°C with an X-band spectrometer with 100 kc field modulation.

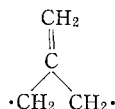
RESULTS AND DISCUSSION

ESR spectra and its Assignment

(1) Methylenecyclopropane

The ESR spectrum obtained from electron-irradiated methylenecyclopropane at -196°C are shown in Fig. 1(a). It is the superposition of three components. The first component is consisted of four lines indicated by black arrows in Fig. 1(a), the detail of which are shown in Fig. 1(b). The second component is a strong center line in Fig. 1(a), the detail of which is shown in Fig. 1(c). The third component indicated by white arrows is a doublet with a coupling constant of about 500 gauss due to the trapped hydrogen atoms.

The wide spread of the first component, up to 500 gauss, cannot be interpreted by the hyperfine structure of usual hydrocarbon free radicals. Recently, Dowd have observed the ESR spectrum of trimethylenemethane (1) formed by photolysis of 4-methylene-*d*¹-pyrazoline.²⁾ He interpreted reasonably a wide spread spectrum as due to the biradical (1) in the ground triplet state. The first component in Fig. 1(a) has just the same spectral shape as that reported by Dowd. Therefore it is attributed due to the biradical (1). As shown in Fig. 1(b), each line of the first component has a hyperfine septet structure with a coupling constant of about 10 gauss. This hyperfine structure may support the above assignment, as the biradical (1) has equevalent six protons interacting with unpaired electrons. The spin density on each methylene carbon atoms was obtained by valence bond calculation, being $+5/12$,³⁾ which gives the proton hyperfine coupling constant of 9.6 gauss. This value is in good agreement with the observed one. The second component shown in Fig. 1(c) is a septet with a coupling constant of about 15 gauss, which may be attributed to an allylic radical (2).



Electron Spin Resonance Study

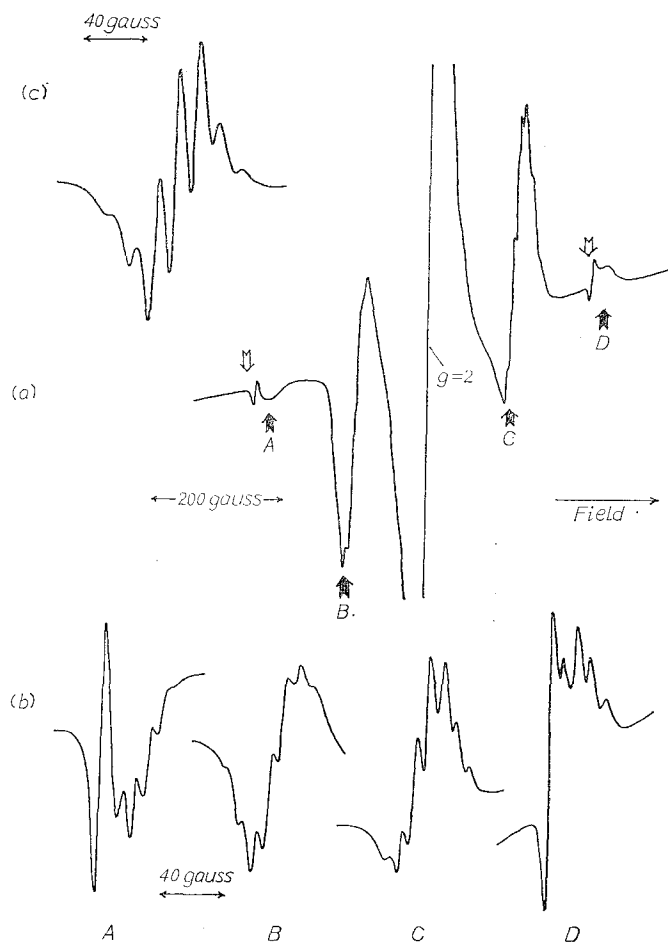


Fig. 1. ESR spectrum obtained from electron-irradiated methylenecyclopropane at -196°C .
 (a) Whole spectrum.
 (b) Detail spectra of the parts indicated A, B, C, D in (a).
 (c) Detail spectrum of the central signal in (a).

The reaction of methylenecyclopropane with methyl radicals gives the same spectra as that shown in Fig. 1(c). The spectrum is, therefore, attributed to the allylic radical (2).

The reaction of methylenecyclopropane with hydroxy radicals gives a spectrum as shown in Fig. 2(a) immediately after the photo-illumination. The spectrum changes its shape to that shown in Fig. 2(b) even at -196°C . This implies the formation of free radicals unstable at -196°C . The spectral shape is too complex to be assigned. The ultraviolet-irradiated pure methylenecyclopropane shows the same spectrum as shown in Fig. 2.

(2) Methylenecyclobutane

From methylenecyclobutane, both the electron irradiation and the reaction with methyl radicals give a spectrum as shown in Fig. 3, except that the former

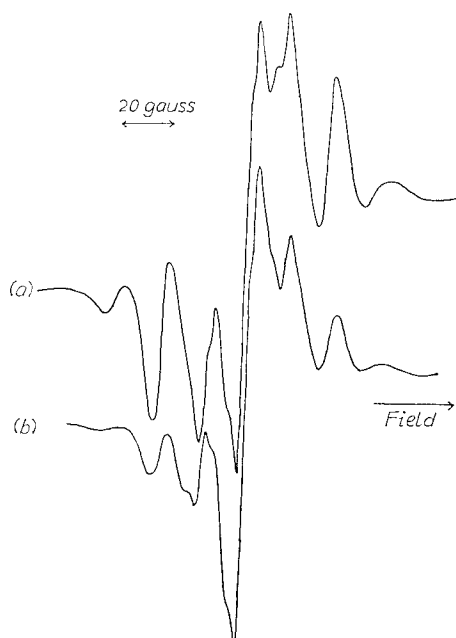


Fig. 2. ESR spectra obtained from the photo-illuminated solid solution of methylenecyclopropane with a few per cent hydrogenperoxide at -196°C .
 (a) Immediately after illumination.
 (b) After 20 hours standing at -196°C .

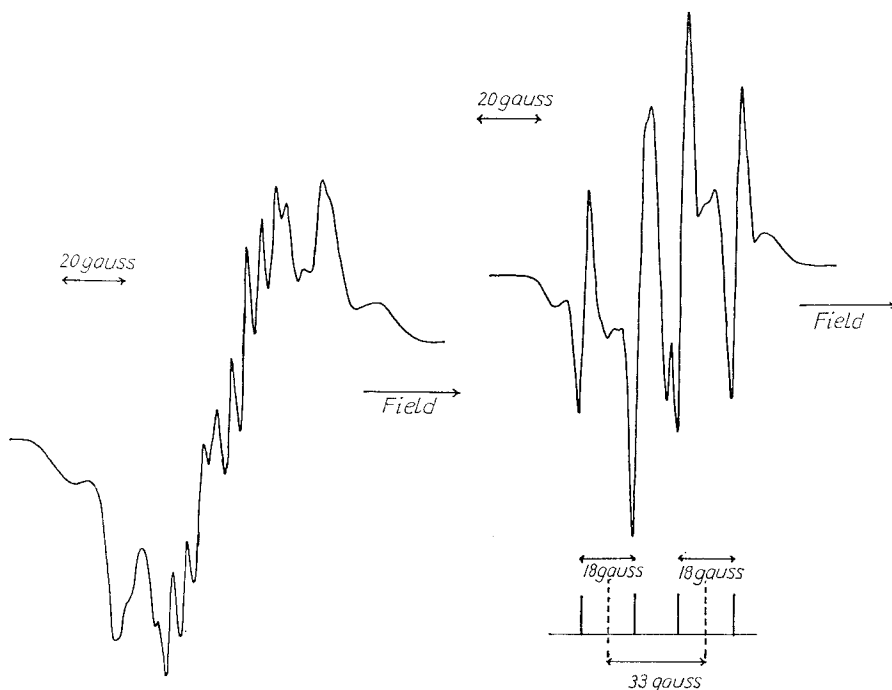
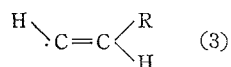


Fig. 3. ESR spectrum obtained from the photo-illuminated solid solution of methylenecyclobutane with a few per cent methyl iodide at -196°C .

Fig. 4. ESR spectrum obtained from ultraviolet-irradiated methylenecyclobutane at -196°C .

gives additionally the doublet spectrum due to hydrogen atoms. The spectrum is the superposition of a sharp component with more than ten hyperfine lines of a coupling constant of about 5 gauss and a broad component of complex shape. The former component having a small coupling constant and large number of hyperfine lines is necessarily due to free radicals with conjugated double bonds, though the structure of the free radicals is not yet understood.

The ultraviolet-irradiation and the reaction with hydroxy radicals give the identical spectrum as shown in Fig. 4, which is composed of two components. One is a well resolved double-doublet spectrum with a coupling constants, 33 and 18 gauss. This hyperfine structure is well interpreted by the structure of free radical (3), according to the hyperfine coupling constant of vinyl radical reported by Fessenden and Schuler.⁴⁾ The observed coupling constant of α -proton, 18 gauss, and that of *cis* β -proton, 33 gauss, are in good agreement with the reported values, 16 and 34 gauss, respectively. Another component is rather weak and not well resolved, so that it is hard to be assigned.



(3) Methylenecyclopentane

The electron-irradiation, the reaction with methyl and hydroxy radicals give the identical spectrum as shown in Fig. 5(a). It is quintet with a coupling constant of about 15 gauss. The hyperfine structure indicates that the spectrum is due to free radical having four equivalent protons, and therefore to the free radical (4) formed by abstraction of one of α -hydrogen atoms adjacent to the double bond. One of the β -protons and three allylic protons contribute equally to the

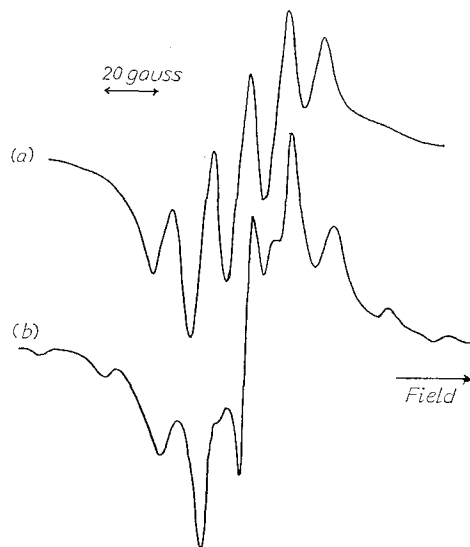
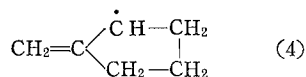


Fig. 5. ESR spectra of methylenecyclopentane radical at -196°C .

(a) Obtained from photo-illuminated solid solution with a few per cent methyl iodide.

(b) Obtained from ultraviolet irradiated sample.

hyperfine interaction.



An alternative assignment may be free radicals formed by bond rupture as $\text{CH}_2=\text{C} \begin{array}{l} \nearrow \text{CH}_2 \cdot \\ \searrow \text{CH}_2-\text{CH}_2 \end{array}$. However, the observed hyperfine coupling constant, 15 gauss, indicates the absence of such a saturated hydrocarbon radicals.

The ultraviolet-irradiation of methylenecyclopentane gives the spectrum as shown in Fig. 5(b), which is very similar to that formed by other three ways.

Mechanism of Radical Formation

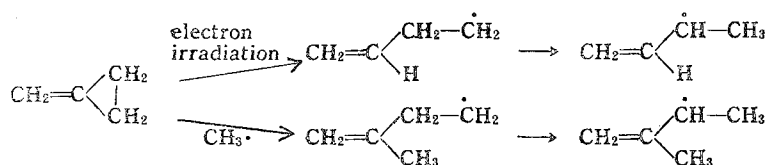
ESR spectra and their assignments mentioned above are summarized in Table 1.

Table 1. The structure of methylenecycloalkane free radicals.

	Electron-irradiation	Reaction with $\text{CH}_3\cdot$	Reaction with $\text{HO}\cdot$	Ultraviolet-irradiation
$\text{CH}_2=\text{C} \begin{array}{l} \nearrow \text{CH}_2 \\ \searrow \text{CH}_2 \end{array}$	Four septet lines $\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ / \quad \backslash \\ \cdot\text{CH}_2 \quad \cdot\text{CH}_2 \end{array}$			Complex spectrum (not to be assigned)
	Septet $\left(\text{CH}_2=\text{C} \begin{array}{l} \nearrow \dot{\text{C}}\text{H}-\text{CH}_3 \\ \searrow \text{R} \end{array} \right)$			
$\text{CH}_2=\text{C} \begin{array}{l} \nearrow \text{CH}_2 \\ \searrow \text{CH}_2 \end{array} \text{CH}_2$	More than 10 h.f. lines (Free radical with conjugated double bond) and Broad spectrum (not to be assigned)			Double-doublet $\left(\begin{array}{c} \text{H} \quad \cdot\text{C}=\text{C} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{H} \end{array} \end{array} \right)$ and Weak unresolved spectrum (not to be assigned)
$\text{CH}_2=\text{C} \begin{array}{l} \nearrow \text{CH}_2-\text{CH}_2 \\ \searrow \text{CH}_2-\text{CH}_2 \end{array}$		Quintet $\left(\text{CH}_2=\text{C} \begin{array}{l} \nearrow \dot{\text{C}}\text{H}-\text{CH}_2 \\ \searrow \text{CH}_2-\text{CH}_2 \end{array} \right)$		

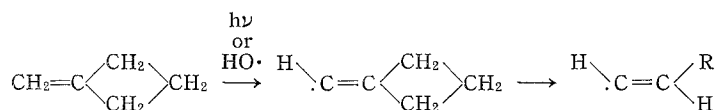
The trimethylenemethane (1) trapped in electron-irradiated methylenecyclopropane is certainly formed by ring opening reaction. This biradical has been implicated as possible intermediate in some reactions of methylenecyclopropane.⁵⁾ In the present investigation, this intermediate is, in fact, observed from the electron-irradiation at low temperature.

A possible mechanism of the allylic radical (2) formation from methylenecyclopropane is as follows:



The carbon-carbon bond adjacent to the double bond is opened by the attack of some free radicals. The attacking free radicals are captured, and then the intramolecular rearrangement of hydrogen atom occurs to result in the formation of the allylic radicals. In the case of electron-irradiation, the attacking free radical is probably hydrogen atoms.

Formation of free radicals with conjugated double bonds from methylenecyclobutane is probably ring opening reaction followed by rearrangements. The formation of the substituted vinyl radical from methylenecyclobutane may be as follows:



The abstraction of one of the methylenic hydrogen atoms is presumably followed by ring opening reaction.

For methylenecyclopropane and methylenecyclobutane, the ring opening reaction of the alkane ring plays an important role in the formation of free radicals, whereas the free radical formation from methylenecyclopentane is only through the abstraction of the hydrogen atom from alkane ring. Such a trend in the type of radical formation reactions is reasonably attributed to the larger strain in the alkane ring with the decreasing number of ring member.

Another interesting finding is that the different ways of radical formation bring about the different types of free radicals. For methylenecyclopropane and methylenecyclobutane the four ways of radical formation are divided into two groups as seen in Table 1: One comprises the electron-irradiation and the reaction with methyl radicals, and the other comprises the ultraviolet-irradiation and the reaction with hydroxy radicals. It is remarkable that the methyl radicals react with methylenecycloalkanes in a different way from hydroxy radicals, though it is remaining unsolved problem to clarify this reason.

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